

Relationship between quantum decoherence times and solvation dynamics in condensed phase chemical systems

Oleg V. Prezhdo* and Peter J. Rossky

*Department of Chemistry and Biochemistry
University of Texas at Austin
Austin, Texas 78712-1167*

Submitted to Phys. Rev. Lett.: February 1, 2008

Abstract

A relationship between the time scales of quantum coherence loss and short-time solvent response for a solute/bath system is derived for a Gaussian wave packet approximation for the bath. Decoherence and solvent response times are shown to be directly proportional to each other, with the proportionality coefficient given by the ratio of the thermal energy fluctuations to the fluctuations in the system-bath coupling. The relationship allows the prediction of decoherence times for condensed phase chemical systems from well developed experimental methods.

PACS numbers: 31.70.Dk, 42.50.Lc, 78.47.+p, 82.20.Wt

Quantum processes in condensed phases are often studied by focusing on a small subset of degrees of freedom and treating the rest as a bath. The subsystem of interest may comprise a single molecule, a molecule plus its nearest surroundings, or even a single vibrational

*Permanent Address: Department of Chemistry, University of Washington, Seattle, WA 98195

mode within a molecule. The remaining degrees of freedom form the bath. In the presence of system-bath interactions, the subsystem’s wave function evolves into a superposition of quantum states. Due to an enormous density of states in a macroscopic environment, small differences in the system-bath coupling lead to rapid divergence between bath evolutions corresponding to different states of the subsystem. The reduced density matrix of the microscopic subsystem, obtained from the total density matrix by integrating over bath degrees of freedom, soon becomes diagonal.¹ Quantum states decohere. The decoherence rate is determined by the sensitivity of bath evolutions to the quantum state of the subsystem. Notably, this sensitivity also determines bath response to a perturbation within the subsystem. In the context of the condensed phase chemical physics, the rate of the solvent bath rearrangements following a perturbation of the solute subsystem is described by a well developed solvent response theory.²⁻⁴ In this Letter, we establish for the first time a quantitative relationship between quantum coherence loss and the short time solvent response.

The new relationship is important because a link between solvation dynamics and decoherence is capable of providing valuable insights into both phenomena. Modern techniques of the solvent response theory employing the concepts of dielectric and mechanical relaxation,^{5,6} and instantaneous normal modes⁴ then become transferable to the description of decoherence. The theory of short-time solvation can benefit from the recent theoretical ideas on quantum Brownian motion^{7,8} and quantum measurement,^{1,9,10} where the notion of decoherence appeared first. Most importantly, currently available experimental means to measure quantum coherence loss¹¹⁻¹³ and short time solvent response^{2,5,14} in a non-equilibrium system can be combined. A relationship between decoherence and solvation time scales further provides a tool to deconvolute the contribution of each effect on observed dynamics. The results presented below form a basis for evaluation of quantum decoherence times in various solute-solvent systems based on the extensive solvent response data accessible from both experimental measurements and adiabatic molecular dynamics simulations.

Following Ref. 15, we consider the direct product of the system S and bath B Hilbert

spaces. For simplicity, the system space is assumed to be two dimensional. We consider two orthogonal states ϕ_1^S and ϕ_2^S of the system and a system-bath interaction that induces quantum transitions in the combined system, with the bath state responding to that of the system:

$$\phi_\alpha^S \otimes \phi_0^B \rightarrow \phi_\alpha^S \otimes \phi_\alpha^B, \quad \alpha = 1, 2, \quad (1)$$

where ϕ_0^B is the initial state of the bath. Transitions from an arbitrary initial system state $c_1\phi_1^S + c_2\phi_2^S$ are then described in terms of the reduced density matrix

$$\begin{pmatrix} |c_1|^2 & c_1 c_2^* \\ c_1^* c_2 & |c_2|^2 \end{pmatrix} \rightarrow \begin{pmatrix} |c_1|^2 & c_1 c_2^* (\phi_2^B | \phi_1^B) \\ c_1^* c_2 (\phi_1^B | \phi_2^B) & |c_2|^2 \end{pmatrix}. \quad (2)$$

Decoherence is defined¹ as decay of the non-diagonal matrix elements, which, for the reduced density matrix of Eq. (2), is clearly determined by the decay of the inner product of the bath states $(\phi_1^B | \phi_2^B)$. Initially, the bath wave functions coincide: $\phi_1^B = \phi_2^B = \phi_0^B$. Later on, the bath wave functions correlated with the different states of the system diverge, and the overlap integral decreases. It is not the decay of the non-diagonal matrix elements *per se* that is most important from the practical point of view, but rather it is the associated slowing down of quantum transitions,^{15–17} known as the quantum Zeno effect in the limit of infinitely fast decoherence.¹⁷ The life time of the quantum state in the presence of a bath varies inversely with the decoherence time. This result follows from the Fermi golden rule in the spin-boson model, where the bath is treated as a set of harmonic oscillators,^{18,19} or in the frozen Gaussian formulation,^{20–22} where the bath wave function is approximated by a set of Gaussian wave packets.²³ Within this Gaussian wavepacket approximation, the average decay of the overlap integral and corresponding non-diagonal matrix elements in Eq. (2) is described by the decoherence function given by Eq. (39) of Ref. 22

$$D(t) = (\phi_1^B | \phi_2^B) = \exp \left[- \left\langle \sum_n \frac{\Delta F_n^2}{4a_n \hbar^2} \right\rangle t^2 \right], \quad (3)$$

where $\Delta F_n = F_{1n} - F_{2n}$ is the expectation value of the difference in the quantum forces experienced by the n th bath degree of freedom, and the angular brackets indicate thermal

averaging. We note that here we do not consider the dynamical effect of the bath on the subsystem energy eigenvalues. In the presence of bath induced fluctuations in these values, a standard pure dephasing contribution (see Refs. 22, 24) to the decay of the off-diagonal elements of the reduced density matrix can potentially contribute as well. In the adiabatic representation the forces are given by the Hellmann-Feynman theorem

$$F_{\alpha n} = (\phi_\alpha^S | \nabla_n H | \phi_\alpha^S), \quad \alpha = 1, 2. \quad (4)$$

In the low temperature regime the width $a_n^{-1/2}$ of the Gaussian wave packet equals the width of the coherent state of a corresponding harmonic oscillator, i.e., $a_n = m_n \omega_n / \hbar$. For higher temperatures, the width of the wave packet incorporates quantum thermal ensemble averaging. The thermal width is analytic for harmonic baths

$$a_n = \frac{m_n \omega_n}{\hbar} \tanh \left(\frac{\hbar \omega_n}{2 k_B T} \right). \quad (5)$$

For arbitrary baths, the width can be defined via the thermal de Broglie wave length $\lambda_B = (2\pi\hbar^2/mk_B T)^{1/2}$. An alternative expression for the thermal width is derived in Ref. 20, Sec. IV by comparing the exact and Gaussian wave packet results for the transition rate in a double well system

$$\begin{aligned} a_n &= \frac{m_n \omega_n}{\hbar} A_n, \\ A_n &= \left[\coth \left(\frac{\hbar \omega_n}{2 k_B T} \right) - \frac{2 k_B T}{\hbar \omega_n} \right]^{-1}. \end{aligned} \quad (6)$$

This expression reduces to the coherent state width in the low temperature case, and gives

$$a_n = \frac{6 m_n k_B T}{\hbar^2} \simeq \left(\frac{\lambda_B}{6} \right)^{-2}, \quad (7)$$

in the high temperature limit. The last formula is particularly useful, since it yields a width which is independent of the frequency; Eq. (7) is designed²⁰ for use in molecular dynamics simulations, where thermal averaging over bath states is performed classically.

Turning to solvation dynamics, the response of the solvent bath to a quantum transition within the solute subsystem is quantified by the normalized correlation function C of the energy gap U between the two quantum states.^{5,25} The fluctuation-dissipation theorem relates the non-equilibrium solvent response to the regression of fluctuations δU of the gap U in equilibrium

$$C(t) = \frac{\langle \delta U(t) \cdot \delta U(0) \rangle}{\langle (\delta U)^2 \rangle}. \quad (8)$$

The short time solvation dynamics that is of relevance in the present discussion depends solely on the change in the solute-solvent coupling due to the quantum transition. The microscopic *short time* expression for $C(t)$ has been obtained in Ref. 25 [Eqs. (2.18), (2.19)] by expanding $C(t)$ in a set of independent modes and in time, yielding

$$C(t) = \exp \left[-\frac{k_B T}{2\langle (\delta U)^2 \rangle} \left\langle \sum_n (U'_n)^2 \right\rangle t^2 \right], \quad (9)$$

where U'_n is the derivative of U with respect to the n th mass-weighted solvent coordinate

$$U'_n = m_n^{-1/2} \frac{dU}{dx_n} = m_n^{-1/2} \Delta F_n. \quad (10)$$

The decoherence τ_D and Gaussian solvation τ_g time scales are given by the variances of the decoherence $D(t)$ and solvent response $C(t)$ functions of Eqs. (3) and (9), respectively. The structure of the equations is clearly similar, and by comparison we obtain

$$\left[\frac{\tau_D}{\tau_g} \right]^2 = \frac{2k_B T}{\langle (\delta U)^2 \rangle} \frac{\sum_n \Delta F_n^2 (m_n)^{-1}}{\sum_n \Delta F_n^2 (a_n \hbar^2)^{-1}}. \quad (11)$$

With the high temperature limit expression for the width [Eq. (7)] the formula simplifies to

$$\left[\frac{\tau_D}{\tau_g} \right]^2 = \frac{12(k_B T)^2}{\langle (\delta U)^2 \rangle} = \frac{6k_B T}{\lambda}. \quad (12)$$

Here, 2λ is the Stokes' shift, the difference between the equilibrium absorption and emission maxima. Within a linear response regime, λ is related¹⁹ to the fluctuations in the

quantum energy gap by the fluctuation-dissipation theorem: $\langle(\delta U)^2\rangle = 2\lambda k_B T$. Eq. (12) establishes direct proportionality between the short time evolution of decoherence and of solvent response in the high temperature limit for the bath. The proportionality coefficient is determined by the ratio of the thermal energy fluctuations $(k_B T)^2$ to the fluctuations in the system-bath coupling $\langle(\delta U)^2\rangle$. The latter can be expressed in terms of the Stokes' shift in the linear response regime. We note that the dependences are sensible: High temperatures accelerate solvation dynamics, large equilibrium fluctuations in the coupling, as well as large Stokes' shifts, are indicative of fast decoherence.

We note that the relationship between the decoherence and solvation time scales presented above using the Gaussian wave packet approximation for the bath wave function also necessarily pertains to the spin-boson model. The spin-boson Hamiltonian describes a two-level system linearly coupled to a harmonic bath¹⁸

$$H_{SB} = -\frac{1}{2}\hbar\Delta\sigma_x + \frac{1}{2}U_0\sigma_z + \sum_n \left(\frac{1}{2}m_n\omega_n x_n^2 + \frac{p_n^2}{2m_n} \right) + \frac{1}{2}q_0\sigma_z \sum_n c_n x_n, \quad (13)$$

where, U_0 and q_0 are the energy and coordinate displacements between the pair of potential minima, Δ is the intrinsic coupling between the two quantum states, c_n is the system-bath coupling constant, and σ_z , σ_x are the Pauli matrices. The terms containing σ_z describe the energy gap

$$U_{SB} = U_0 + q_0 \sum_n c_n x_n. \quad (14)$$

According to Eqs. (9), (10), the short-time solvent response function of the spin-boson model is

$$C_{SB} = \exp \left[-\frac{1}{2} \frac{k_B T}{\langle(\delta U)^2\rangle} \sum_n \frac{q_0^2 c_n^2}{m_n} t^2 \right]. \quad (15)$$

The decoherence function can be extracted from the Fermi golden rule result for the spin-boson problem [Eqs. (3.35), (3.36) and (3.2) of Ref. 18]

$$D_{SB} = \exp \left[- (q_0^2 / \pi \hbar) Q_2(t) \right], \quad (16)$$

with

$$Q_2(t) = \int_0^\infty \frac{J(\omega)(1 - \cos \omega t)}{\omega^2} \coth(\hbar\omega/2k_B T) d\omega, \quad (17)$$

and

$$J(\omega) = \frac{\pi}{2} \sum_n \frac{c_n^2}{m_n \omega_n} \delta(\omega - \omega_n). \quad (18)$$

The short-time expansion of $Q_2(t)$ gives

$$D_{SB} = \exp \left[-\frac{1}{4} \sum_n \frac{q_0^2 c_n^2}{m_n \hbar \omega_n} \coth(\hbar\omega_n/2k_B T) t^2 \right] \quad (19)$$

$$= \exp \left[-\frac{1}{4} \sum_n \frac{q_0^2 c_n^2}{a_n \hbar^2} t^2 \right], \quad (20)$$

with a_n as in Eq. (5). The expression in Eq. (20) is a specific case of Eq. (3) with $\Delta F_n = -q_0 c_n$. Comparison of Eqs. (15) and (20) leads to the relationship given in Eq. (11) between the decoherence and Gaussian solvation times.

We can directly test Eq. (12) for the case of relaxation following transition from the first excited to the ground state of the hydrated electron, whose time dependent properties are well studied theoretically (see Refs. 20–22, 26, 27 and references therein). Based on a molecular dynamics trajectory for the first excited state of the hydrated electron,²⁶ the equilibrium energy gap U is 0.56 eV and the fluctuation in the energy gap $\langle (\delta U)^2 \rangle^{1/2}$ is 0.21 eV, which corresponds to a 1.7 eV Stokes' shift (2λ) at room temperature. This Stokes' shift corresponds closely to that found in non-adiabatic simulations.²⁸ The short-time component of the solvent response function $C(t)$ of Eq. (8) is found to be characterized by a 10.6 fs Gaussian time scale, τ_g . From these data, the decoherence time τ_D of the first excited state of the hydrated electron calculated via Eq. (12) is 4.5 fs. This estimate falls within the previously reported range of 2.7–5.1 fs,^{20–22} with the value of 5.1 fs obtained in the high temperature approximation for Eq. (6).

The properties of the solute and the nature of the quantum transition define the difference in the solute-solvent potential for the initial and final states and, therefore, determine the

magnitude of the Stokes’ shift in the relationship (12) between the decoherence and solvation times. Intrinsic solvent properties also, to some extent, affect the magnitude of the Stokes’ shift. However, the major solvent influence on the duration of quantum coherence is due to solvent’s ability to respond to a perturbation in the solute, i.e. as reflected in the rate of solvent response, τ_g . Based on the success above for the hydrated electron, one can address other systems, which will demonstrate the variability of decoherence times. For a styryl dye in methanol,²⁹ experiment yields an estimated τ_g of 40 fs and a Stokes’ shift of 115 nm yielding a decoherence time of 6.8 fs. Acetonitrile [CH₃-CN], the next solvent in a logical series exhibits a 100 fs experimental short time solvent response.³⁰ Simulation of the electronic transition of the betaine-30 molecule in acetonitrile is characterized by a similar 91 fs short-time solvation.³¹ The value for τ_g , together with the 0.16 eV electronic energy gap fluctuation evaluated along the ground state trajectory,³¹ leads via Eq. (12) to a substantially longer 49 fs decoherence time. Compared to the protic solvents, acetonitrile is much less effective in destroying quantum coherence.

In summary, we have presented an analytical relationship between the time scale for quantum decoherence and that governing the short time response of solvent to a perturbation in the solvent-solute coupling. The proportionality constant relating these requires knowledge of only the Stokes’ shift associated with the change in solute state. The expression successfully reproduces results obtained directly by other routes, allows the prediction of decoherence times for other solution systems. It is expected that since the required input data is becoming readily accessible experimentally for even the most rapidly responding condensed phase environments, the derived relation will be very valuable to advancing the study of both decoherence and condensed phase chemical dynamics more generally.

Acknowledgment: The authors are grateful to the National Science Foundation (CHE-9314066) for support of the research reported here. OVP acknowledges the support of the Hemphill/Gilmore fellowship fund.

References

- [1] W. H. Zurek, Progress of Theor. Phys. **89**, 281 (1993).
- [2] M. Maroncelli, J. Mol. Liquids **57**, 1 (1993).
- [3] R. M. Stratt and M. Maroncelli, J. Phys. Chem. **100**, 12981 (1996).
- [4] R. E. Larsen, E. F. David, G. Goodyear, and R. M. Stratt, J. Chem. Phys. **107**, 524 (1997).
- [5] M. Maroncelli, J. MacInnis, and G. R. Fleming, Science **243**, 1674 (1989).
- [6] *Activated Barrier Crossing*, edited by G. R. Fleming and P. Hanggi (World Scientific, NJ, 1993).
- [7] W. G. Unruh and W. H. Zurek, Phys. Rev. D **40**, 1071 (1989).
- [8] B. L. Hu, J. P. Paz, and Y. Zhang, Phys. Rev. D **47**, 1576 (1993).
- [9] L. Diósi, N. Gisin, J. Halliwell, and I. Percival, Phys. Rev. Lett. **74**, 203 (1995).
- [10] M. Gell-Mann and J. B. Hartle, Phys. Rev. D **47**, 3345 (1993).
- [11] M. H. Vos, F. Rappaport, J.-C. Lambrey, J. Breton, and J.-L. Martin, Nature **363**, 320 (1993).
- [12] K. Wynne and R. M. Hochstrasser, Chem. Phys. **171**, 179 (1993).
- [13] G. R. Fleming and R. van Grondelle, Phys. Today **47**, 48 (1994).
- [14] P. F. Barbara and W. Jarzeba, Adv. Photochem. **15**, 1 (1990).
- [15] M. Simonius, Phys. Rev. Lett. **40**, 980 (1978).
- [16] A. J. Bray and M. A. Moore, Phys. Rev. Lett. **49**, 1545 (1982).

- [17] M. Berry, in *Fundamental Problems in Quantum Chemistry; a conference held in honor of Professor John A. Wheeler. Annals of the New York Academy of Sciences*, edited by D. M. Greenberger and A. Zeilinger (The New York Academy of Sciences, New York, NY, 1995), Vol. 755, pp. 303–317.
- [18] A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, *Rev. Mod. Phys.* **59**, 1 (1987).
- [19] M. Cho and R. J. Silbey, *J. Chem. Phys.* **103**, 595 (1995).
- [20] E. Neria and A. Nitzan, *J. Chem. Phys.* **99**, 1109 (1993).
- [21] B. J. Schwartz, E. R. Bittner, O. V. Prezhdo, and P. J. Rossky, *J. Chem. Phys.* **104**, 5942 (1996).
- [22] O. V. Prezhdo and P. J. Rossky, *J. Chem. Phys.* **107**, 5863 (1997).
- [23] E. J. Heller, *J. Chem. Phys.* **75**, 2923 (1981).
- [24] A. Staib and D. Borgis, *J. Chem. Phys.* **103**, 2642 (1995).
- [25] R. M. Stratt and M. Cho, *J. Chem. Phys.* **100**, 6700 (1994).
- [26] B. J. Schwartz and P. J. Rossky, *J. Chem. Phys.* **101**, 6902 (1994).
- [27] O. V. Prezhdo and P. J. Rossky, *J. Phys. Chem.* **100**, 17094 (1996).
- [28] S. J. Rosenthal, B. J. Schwartz, and P. J. Rossky, *Chem. Phys. Lett.* **229**, 443 (1994).
- [29] D. Bingemann and N. P. Ernsting, *J. Chem. Phys.* **102**, 2691 (1995).
- [30] S. J. Rosenthal, X. Xie, M. Du, and G. R. Fleming, *J. Chem. Phys.* **95**, 4715 (1991).
- [31] J. Lobaugh and P. J. Rossky, unpublished.